2018 DOE Vehicle Technologies Office Annual Merit Review

SEI Stabililzation (SEISta)

Chemical Reactivity of Silicon at the Surface

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Project ID BAT345

Overview

Timeline

- October 1st 2016 - September 30st 2019.
- Percent complete: 40%

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

Budget

- Funding for FY 18: $3900K

Partners

- Five Laboratory Team lead by NREL:
  - Sandia National Laboratory
  - Argonne National Laboratory
  - Oak Ridge National Laboratory
  - Lawrence Berkeley National Laboratory
- UC Berkeley
- Colorado University Boulder
- Colorado School of Mines
- University of Rhode Isalnd

Program Relevance

Si anodes are ~10x higher capacity than graphite anodes

1. Si anodes have three major challenges to commercialization
   - High Capacity Fade
   - Poor Shelf Life
   - Electrode formulation/stability
2. SEI formation in Si much more complex than in graphite, and seems to be dependent on initial state and history
   - Large volume expansion on alloying
   - Extensive gas formation upon

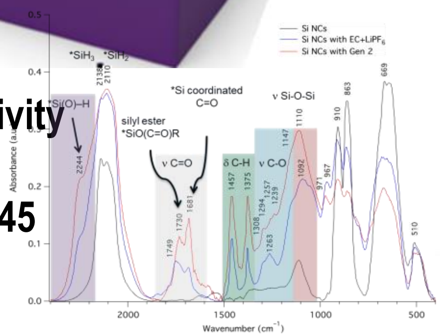
Objective:

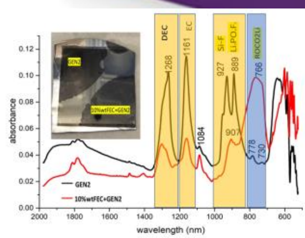
Improve calendar life and understand initial stages of SEI formation by understanding intrinsic chemical reactivity of Si electrodes

Chemical reactivity vs electrochemical reactivity

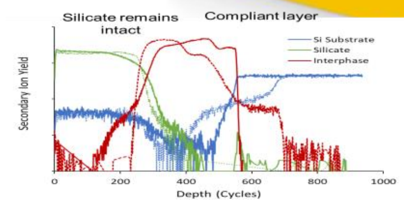
J. Phys. Chem. C 2017, 121, 14476–14483

Chemical Reactivity of Silicon Project ID BAT345



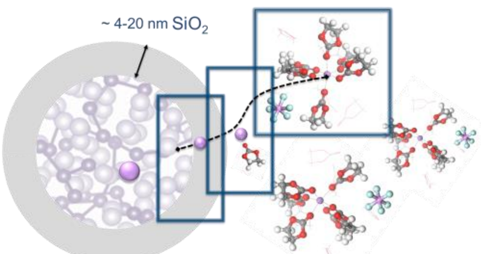


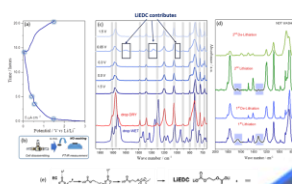
Surface analysis of the Silicon SEI ID BAT347

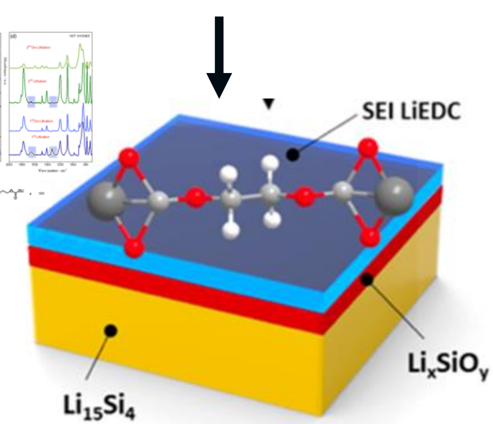


Role of Li Silicates in Si SEI Formation ID BAT348

Spectroelectrochemistry on silicon ID BAT346



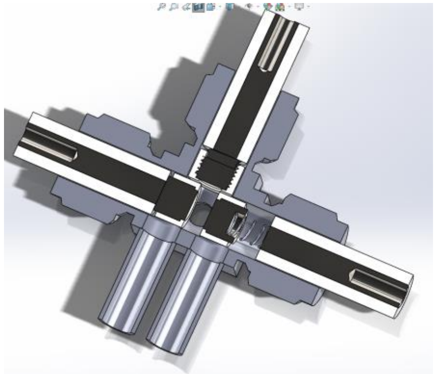




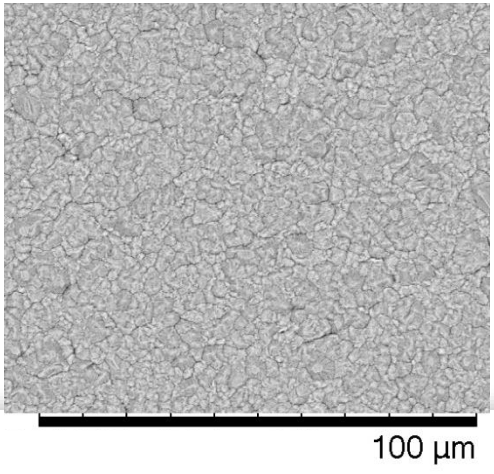
Predicting and Understanding Novel Electrode Materials From First-Principles Project ID BAT344

Approach built on extensive collaboration, standardization of materials, architectures

- Sputtering to grow well defined films (BAT346, 347, 348)
- Homogeneous Si, SiO_x, Li-Si-O particles
- Si wafers (BAT343)



- Standardize test cells (BAT346,347, 348)
- Round Robin type evaluations



Extensive characterization with multiple tools on the same materials (BAT 346, 347)

Milestones FY18

- Quarter 1 Milestone:

Have completed the selection and characterization (XPS, SIMS, IR, and Raman), including determination of the surface termination chemistry and impurity levels, of the SEISta model research samples to be used by all members of the team in FY18. **100% complete**

- Quarter 2 Milestone:

Have characterized (XPS, SIMS, IR, and Raman) the surface chemistry and composition of the SEISta model research samples after contact with the electrolyte, before cycling, including the nature of the electrolyte decomposition products. **100% complete**

- Quarter 3 Milestone:

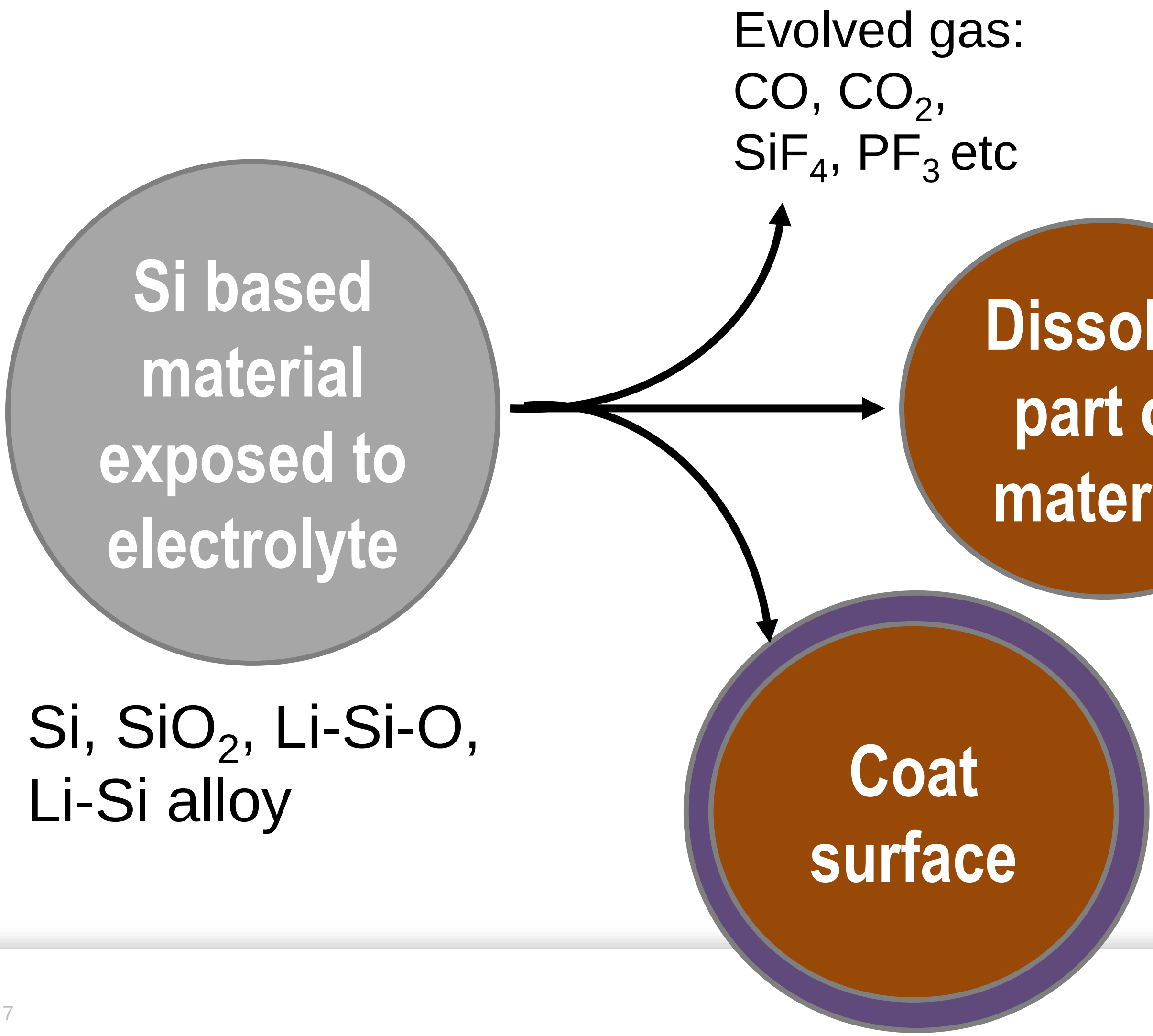
Completed characterization (electrochemistry, IR and Raman) of the early stage silicon electrolyte interphase formation on the SEISta model research samples, specifically by establishing and demonstrating a procedure for quantitatively measuring the solubility of SEI on silicon surfaces.

- Quarter 4 Milestones:

Established and demonstrated a procedure for measuring the growth rate of silicon SEI components at fixed potentials and during cycling.

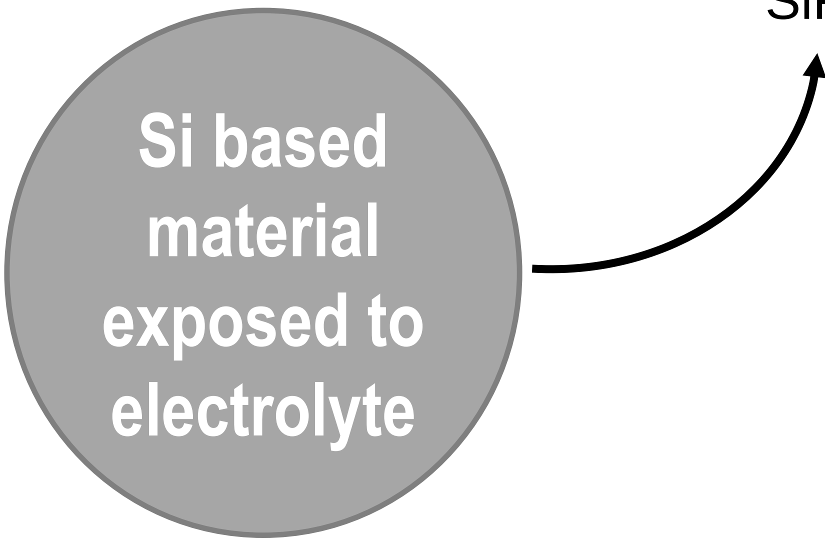
Have determined how the physical properties of the silicon electrolyte interface are influenced by the nature of the silicon surface on the SEISta model samples.

Chemical reactivity of Si is complex but represents earliest stages of SEI formation and sources of capacity loss



Gas evolution when exposed to electrolyte will influence calendar life

Evolved gas:
CO, CO_2,
SiF_4, PF_3 etc

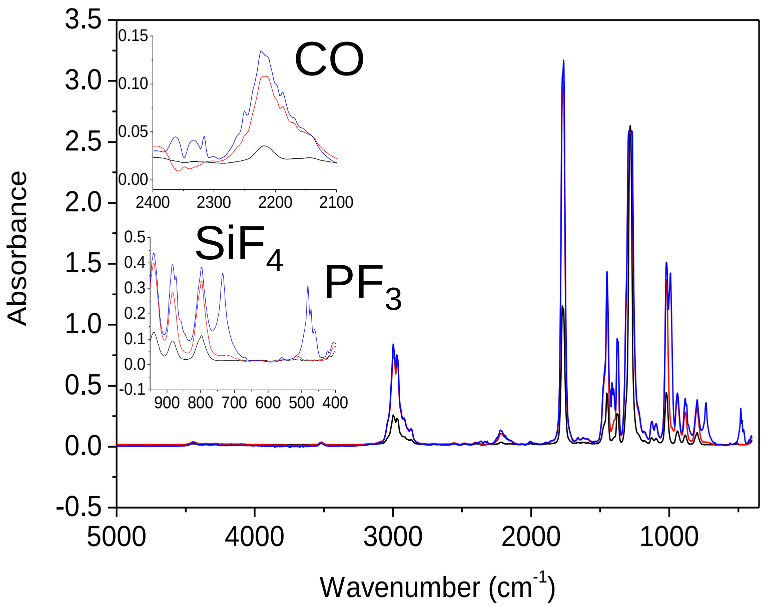


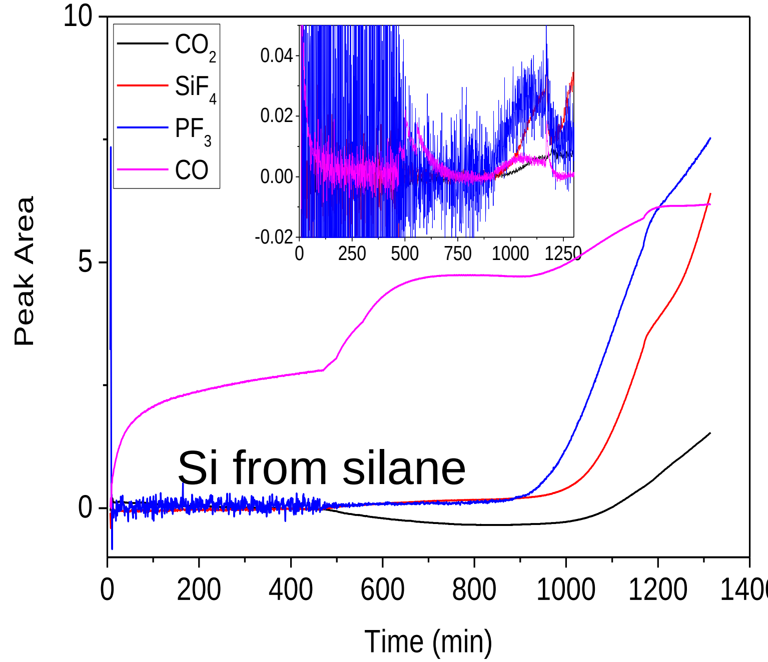
Si, SiO_2, Li-Si-O,
Li-Si alloy

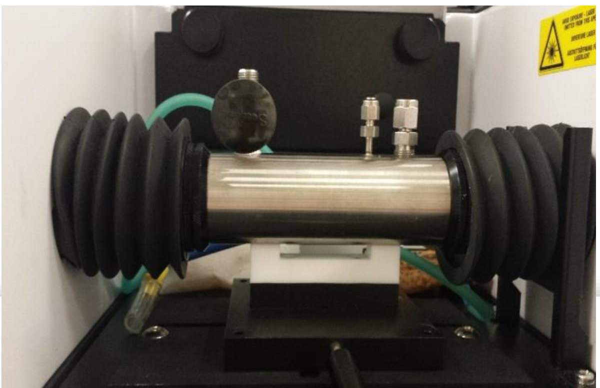
How do these gasses influence SEI formation?

Monitor evolution of gassing and how it changes with material

Gas evolution reactions evolve with time pointing to complex reaction mechanisms (see BAT348 for electrochemistry)



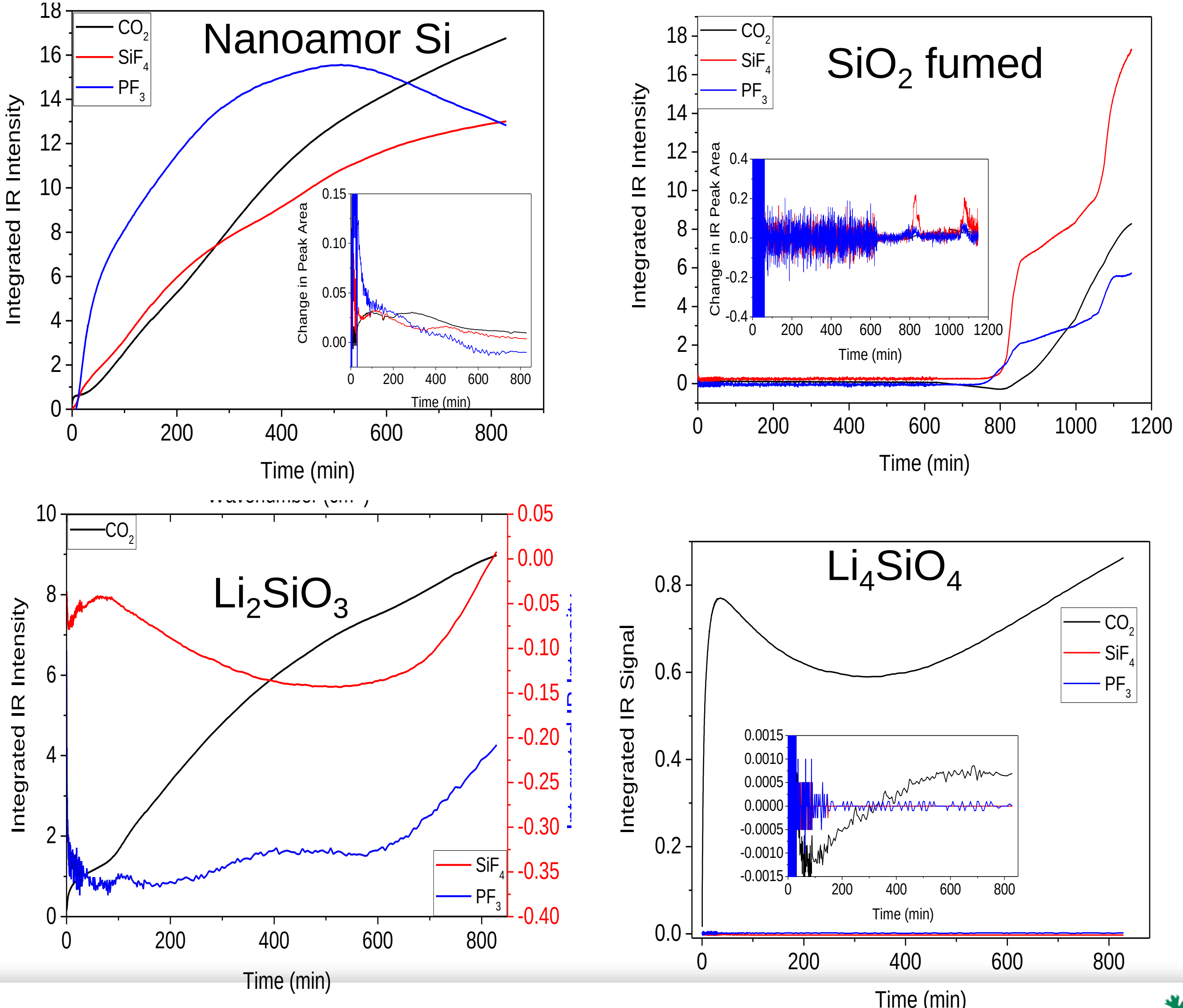




- Gas evolution followed by IR spectroscopy

From 100 μL 1.2M $LiPF_6$ EC/EMC

Rate and type of gas produced depends on electrode material and surface chemistry

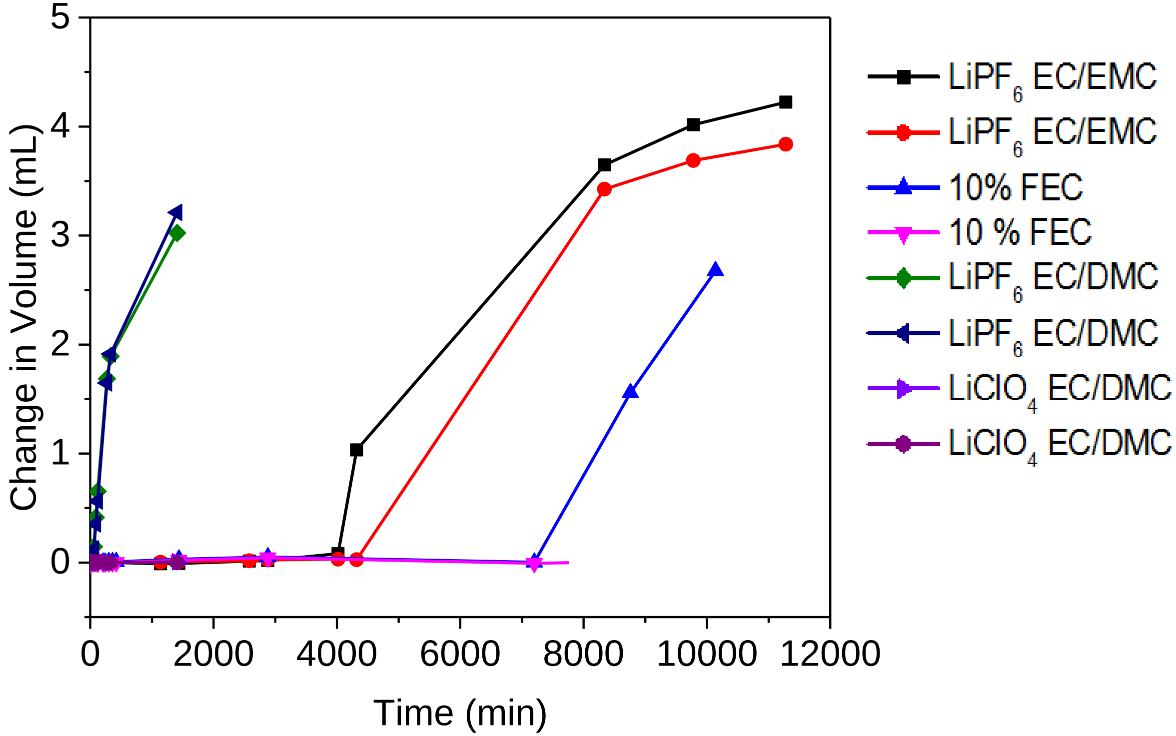


These reactions consume electrolyte and change the surface chemistry influencing SEI formation.

Can we direct surface chemistry to control extent and choice of reactions?

Identified electrolyte dependence of gassing

Choice of salt, solvent, additive all play a complicated role in the reactivity

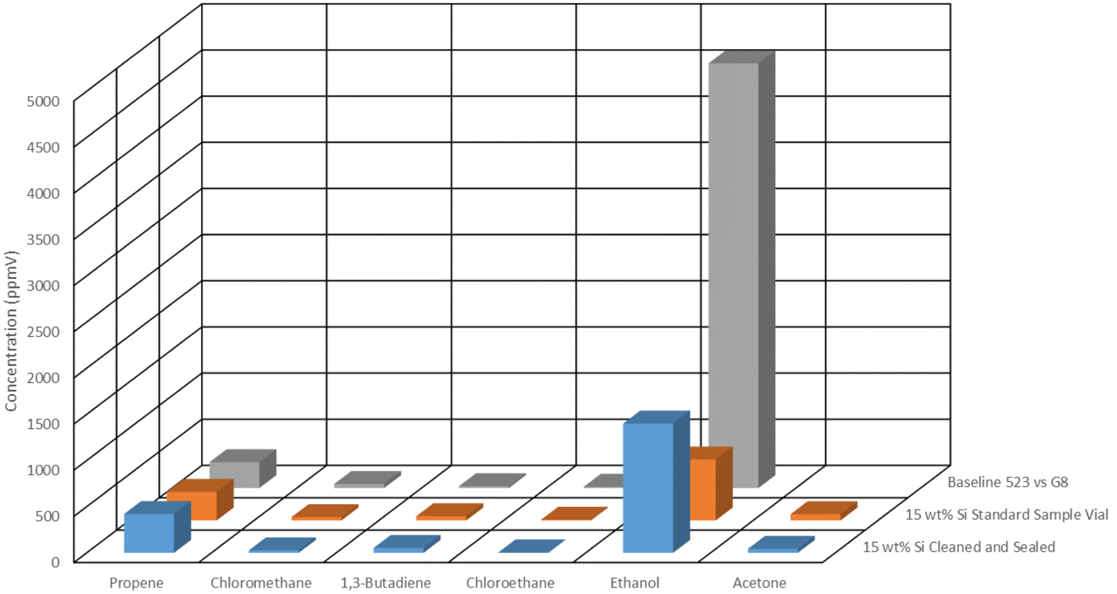


- Example using Nanoamor Si from Si-Deep Dive

Significant gas evolution of explosive gasses shown in calorimetry results

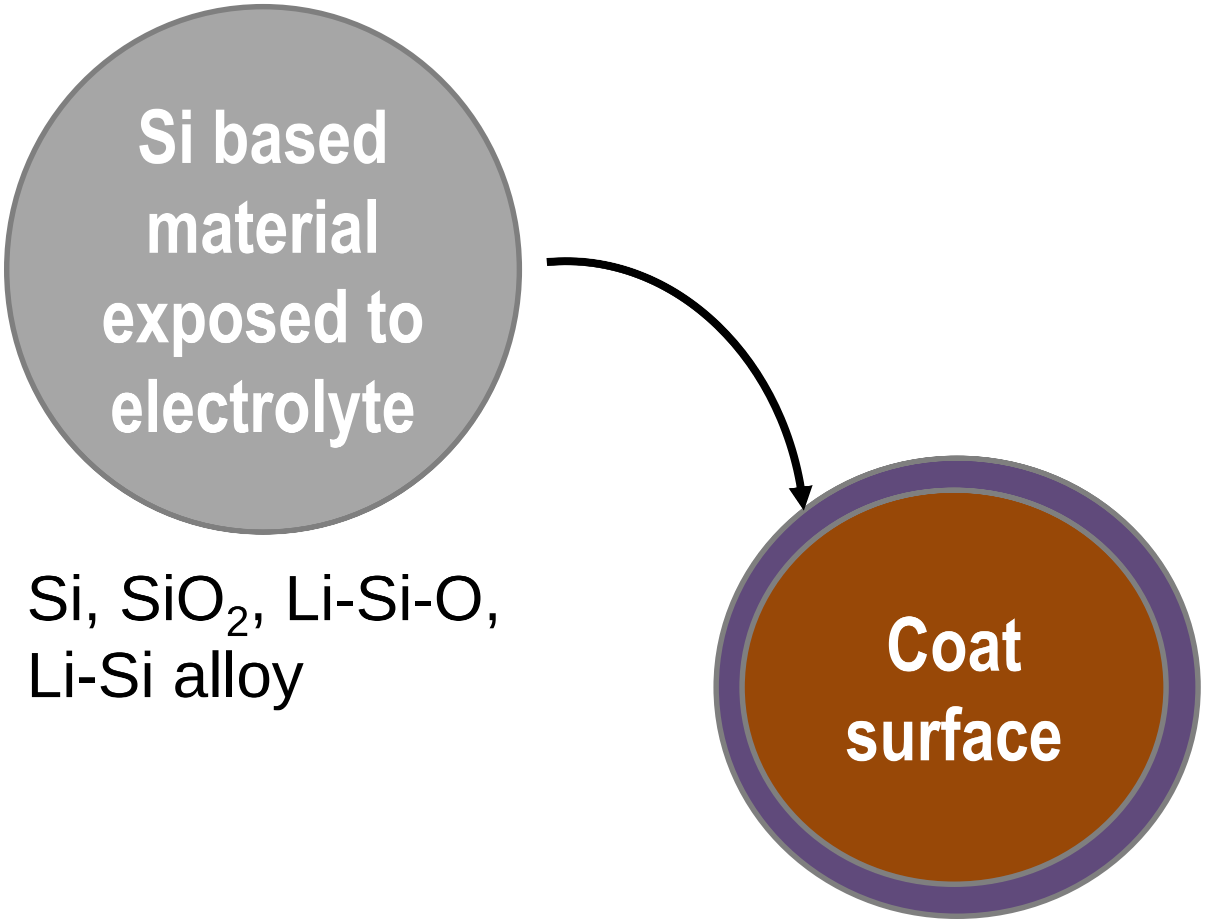
Shows importance of understanding and controlling the surfaces

Complete rupture for entire ARC system seen with nano silicon electrodes at both 10 and 15% Si



Significant evolution of gas related to surface reactivity

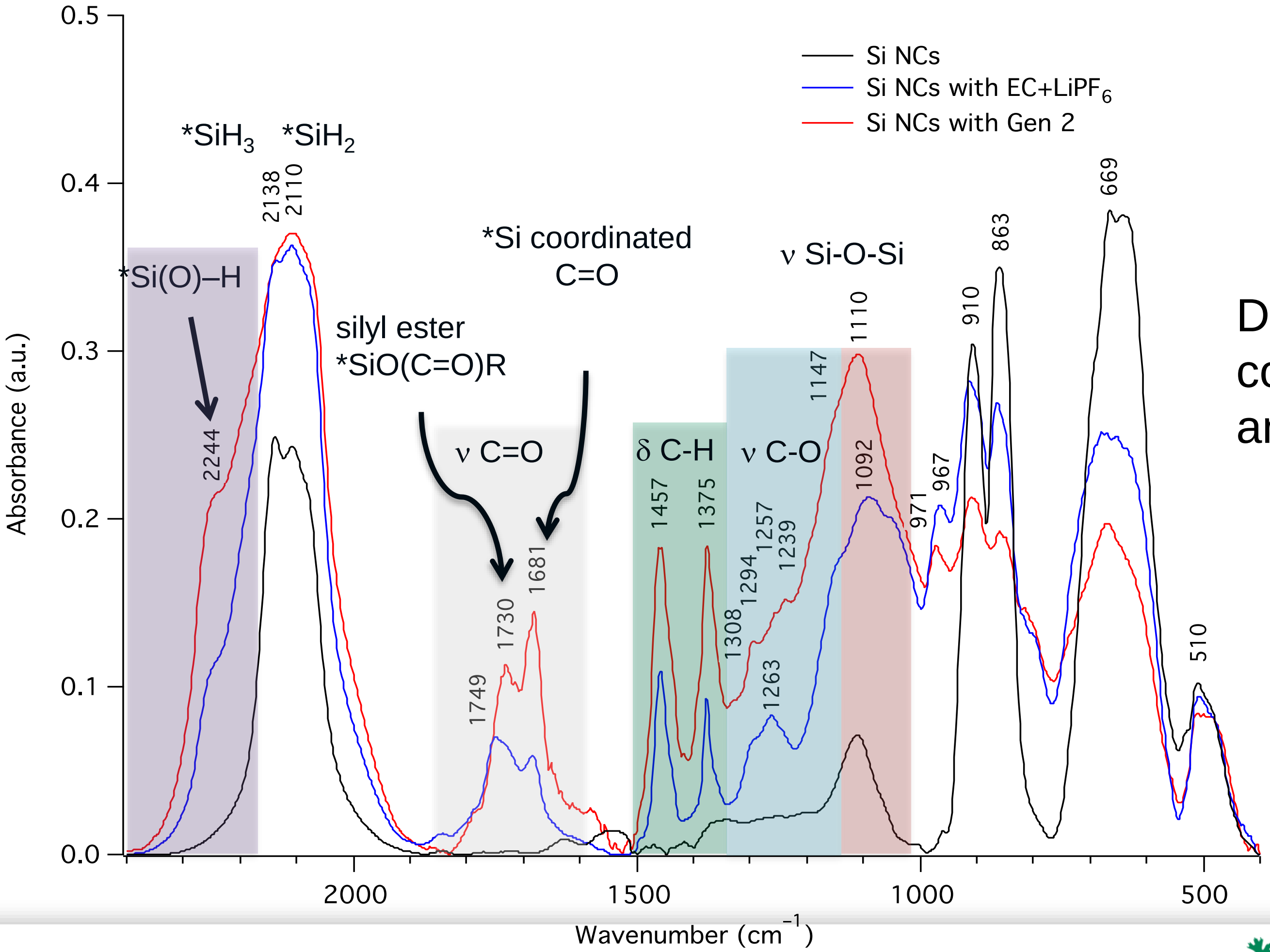
Changing the surface chemistry will control SEI formation, ion transport, chemical reactivity



Si, SiO_2, Li-Si-O, Li-Si alloy

Monitor changes in electrode surface chemistry with exposure to electrolytes

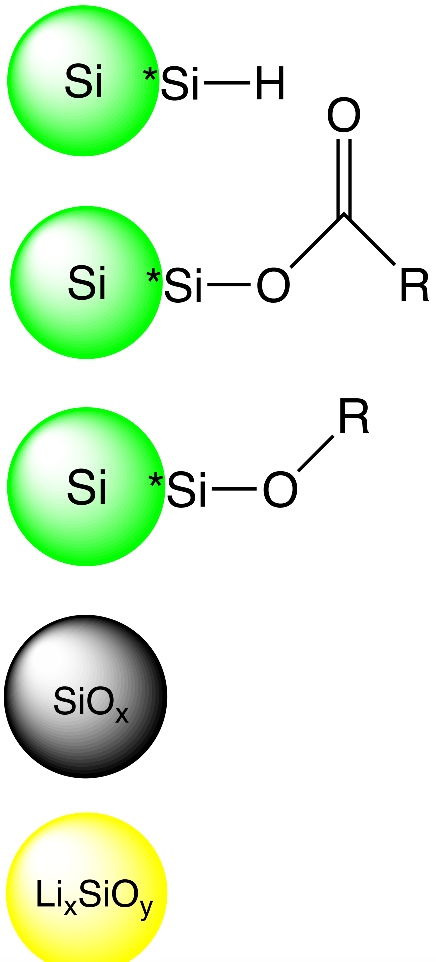
After chemical reaction extensive functionality introduced to materials surface which will change SEI formation reaction processes and ion transport



Data shows growth of covalently bonded C=O and O-C=O species

Monitor changes in chemistry at model electrode surfaces with electrolyte exposure

Demonstrate some surface functionality on Si stable to electrolyte content which points at pathways to stabilize interface



1. Electrolyte soak 1–3 days
2. Wash with polar solvent
3. Recover solid
4. Examine solid via FTIR

(Silicon Hydride) Reactive

(Silyl Ester) Reactive

(Silyl Ether) Stable

(Fumed or NanoAmor SiO_x) Reactive

(Stöber SiO_x) Stable

(Li_2SiO_3) Reactive

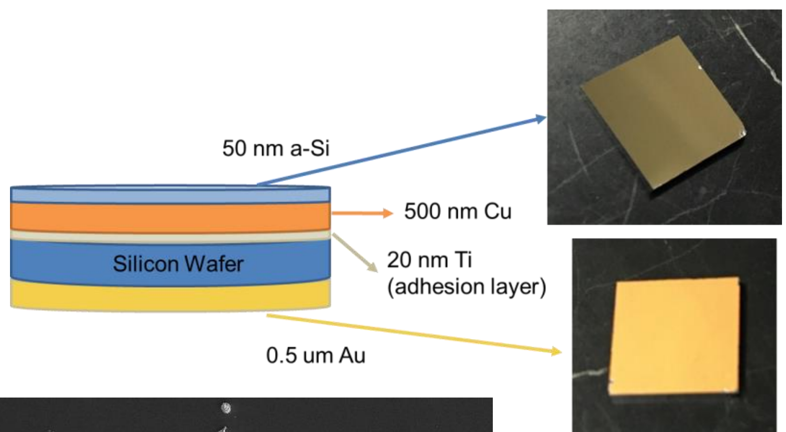
(Li_4SiO_4) Stable

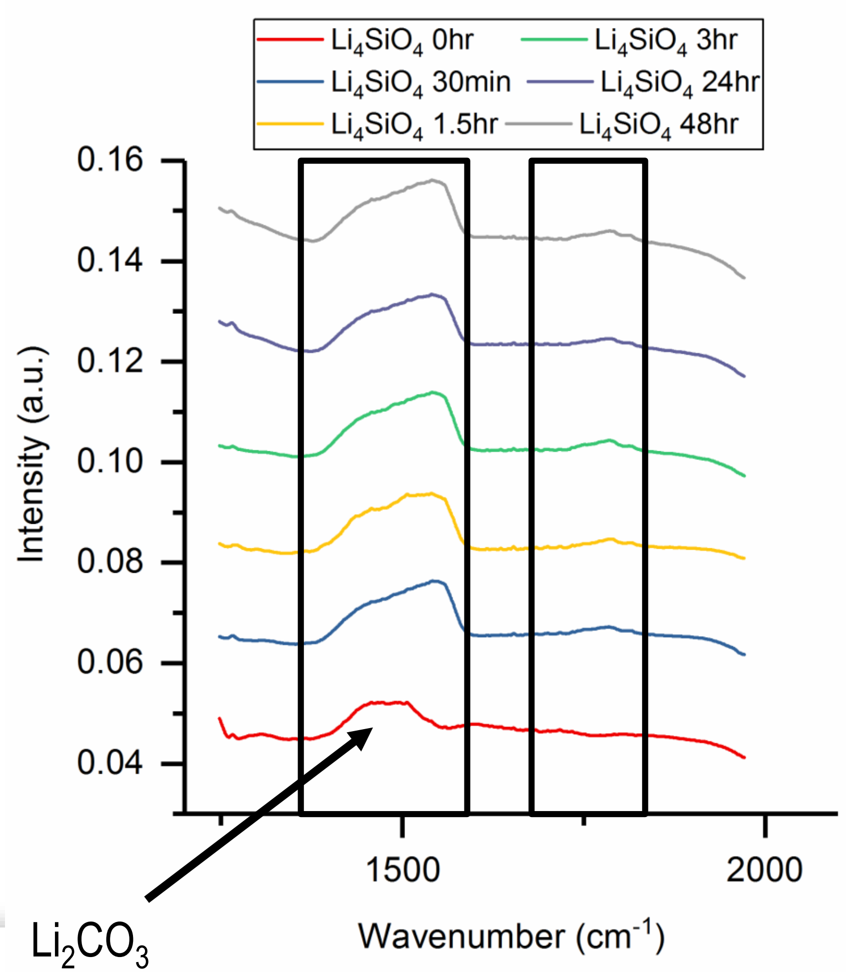
Electrolyte = 1.2 M $LiPF_6$ EC <u>*OR*</u> 1.2 M $LiPF_6$ EC/EMC (3:7)

Oak Ridge National Laboratory
MANAGED BY UT-BATTELLE FOR THE U.S. DEPARTMENT OF ENERGY

Soaking experiments reveal how surface termination of Li-Si-O films evolve with electrolyte exposure

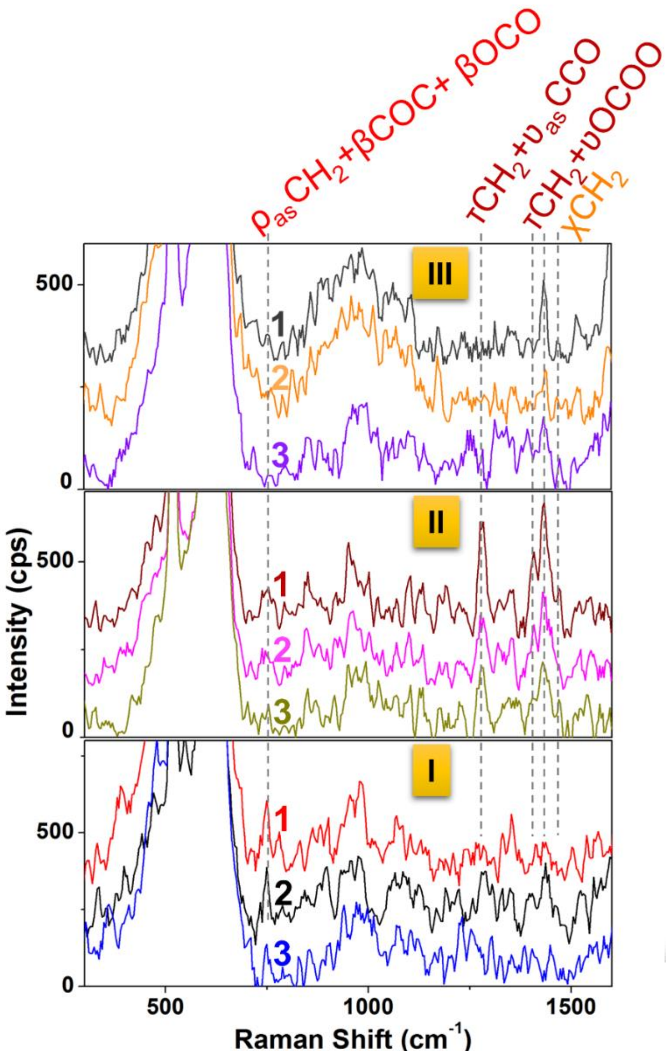
High Li content coatings react to form Li_2CO_3 which will passivate electrodes (BAT348)

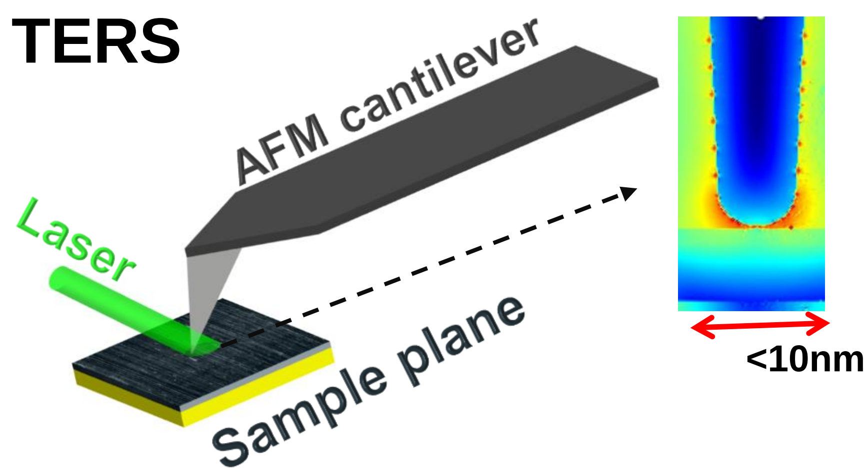


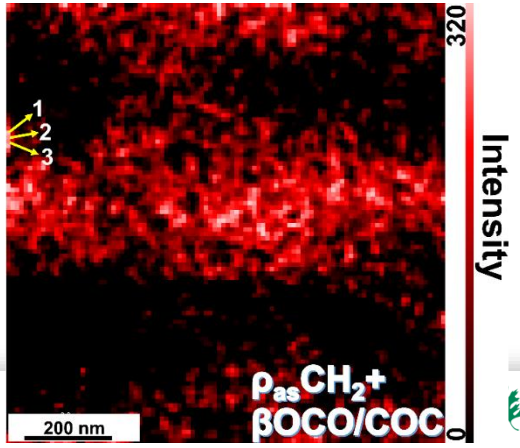


Developed new Tip Enhanced Raman Spectroscopy (TERS) tool to study surfaces

Able to spatially resolve chemical components on an electrode surface that you can't do with normal Raman spectroscopy; compliment FTIR studies (BAT346)

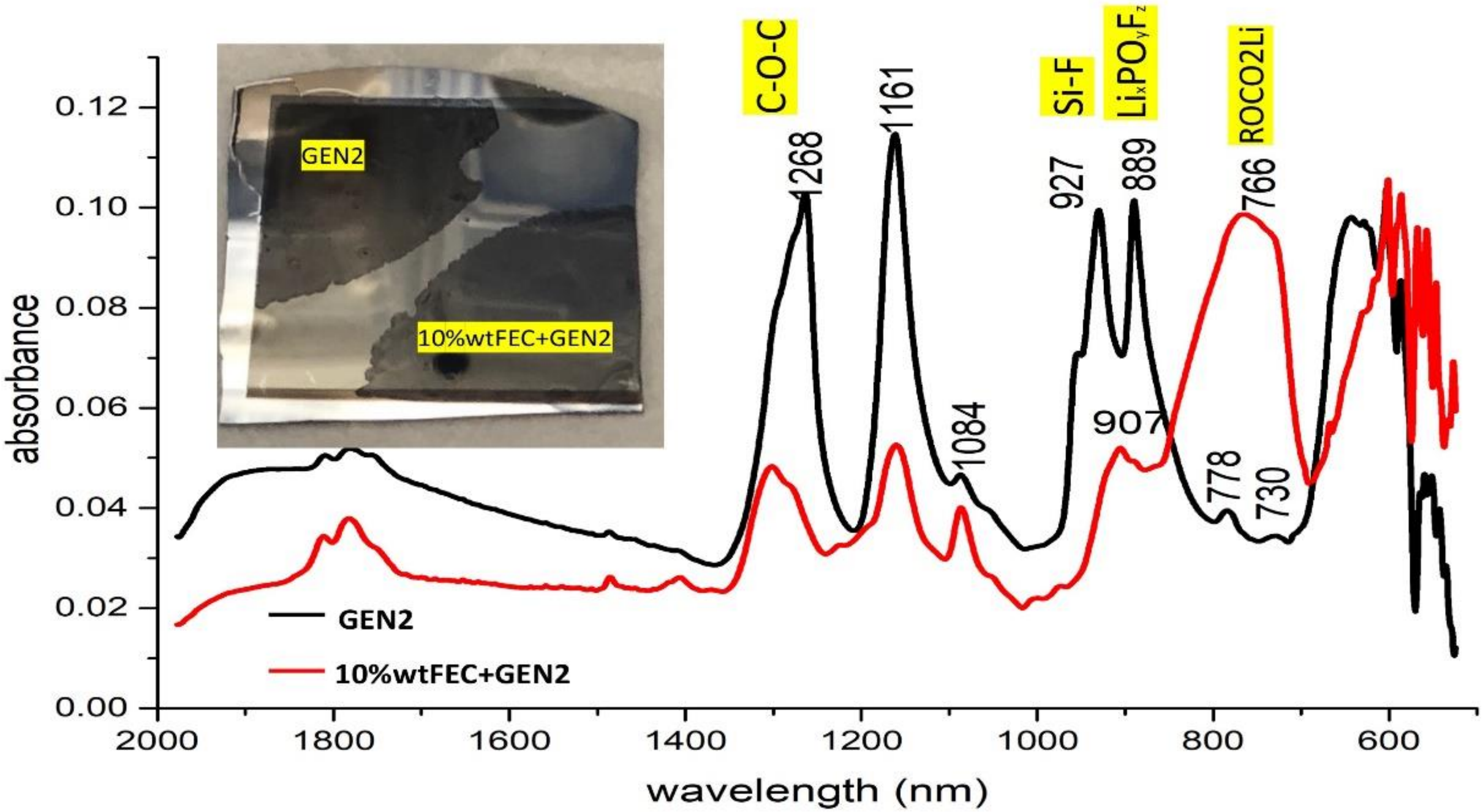






Study reactions with “charged” alloy

Data show Li-Si alloys react differently than unlithiated electrodes which may lead to different SEI chemistry and stability.

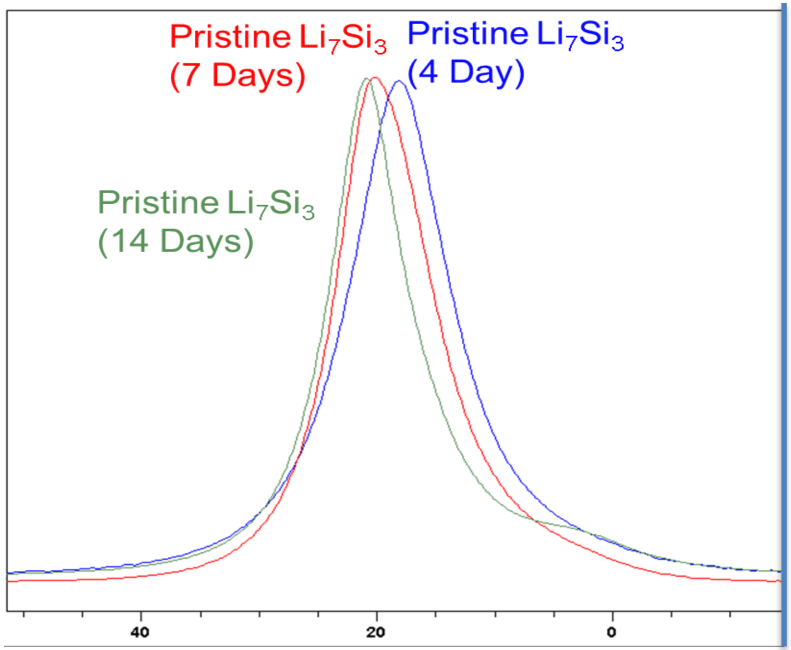


Interestingly the addition of FEC gives a more organic like SEI.

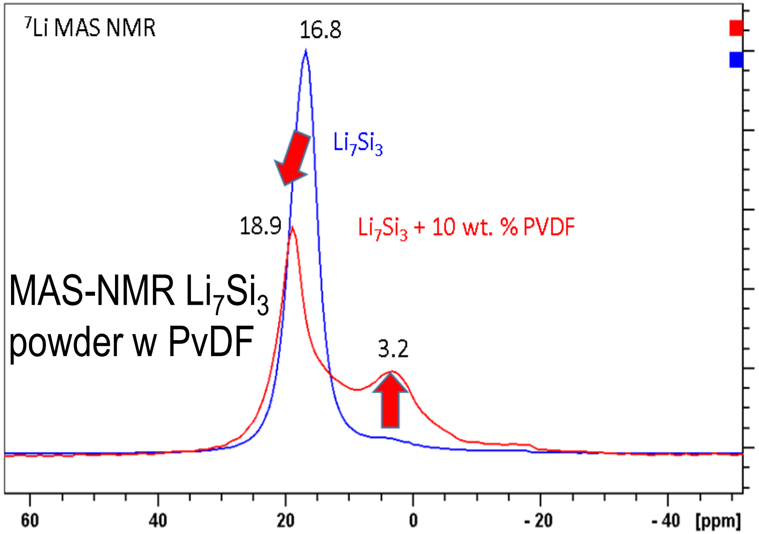
"Charged" alloy material degrades in contact with trace species

Choice of binder will affect electrode stability

Samples age in a static environment



Samples change with PVdF contact



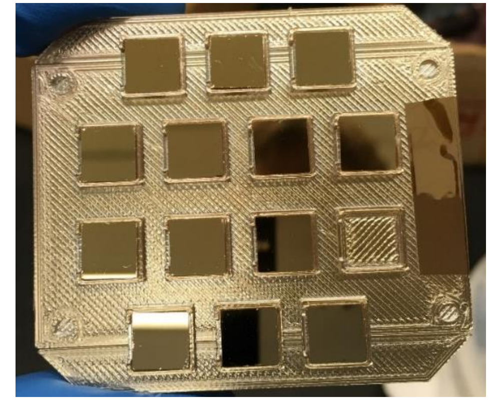
Reactivity studies show reactions of the Li_7Si_3 silicide with (1) trace oxygen, water, or carbon dioxide in the storage boxes results in the samples losing lithium (to $Li_{12}Si_7$) with formation of diamagnetic salt, and (2) rapid reaction of the fresh Li_7Si_3 with PVdF to also give a diamagnetic salt and lower lithium content silicide.

Dissolution of silicon will affect capacity

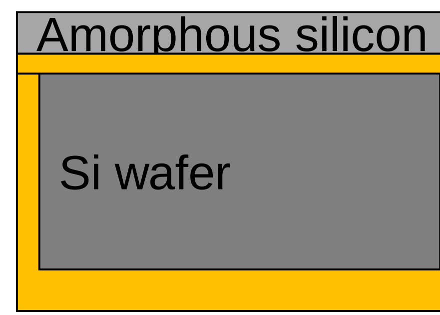
Si based material exposed to electrolyte

Dissolve part of material

Si, SiO_2, Li-Si-O, Li-Si alloy



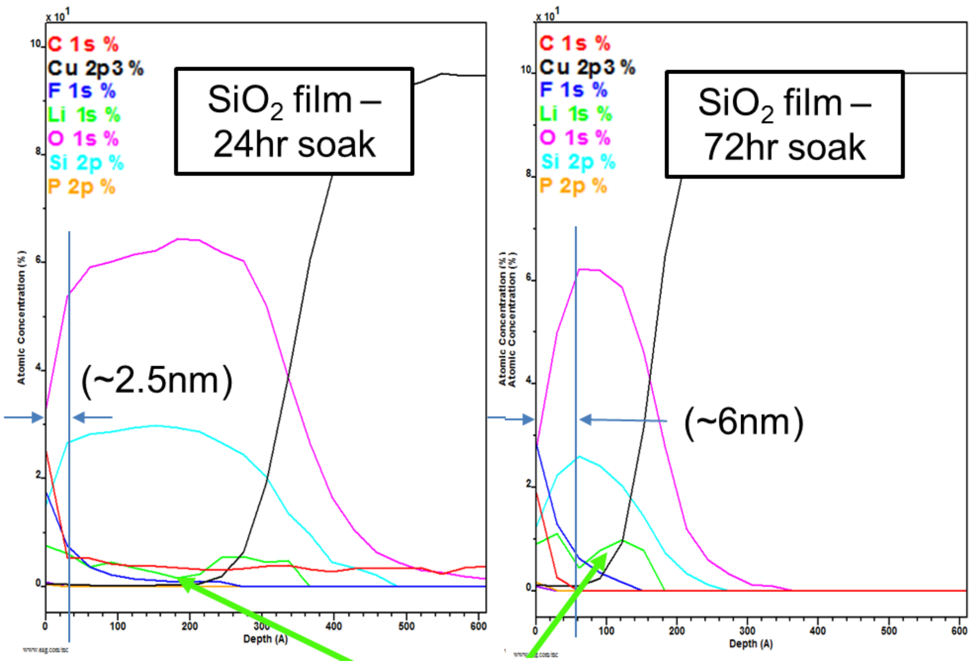
Sputter deposited Si



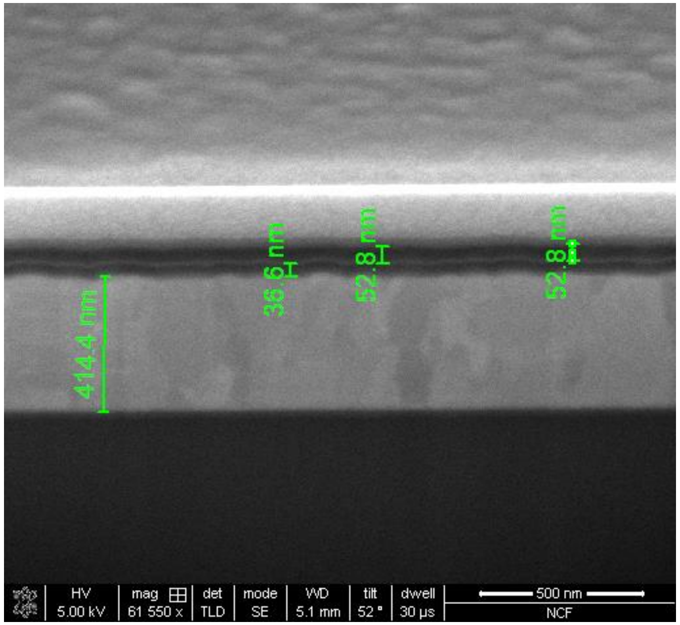
Copper layer

It's not just a change in termination but a change in layer thickness

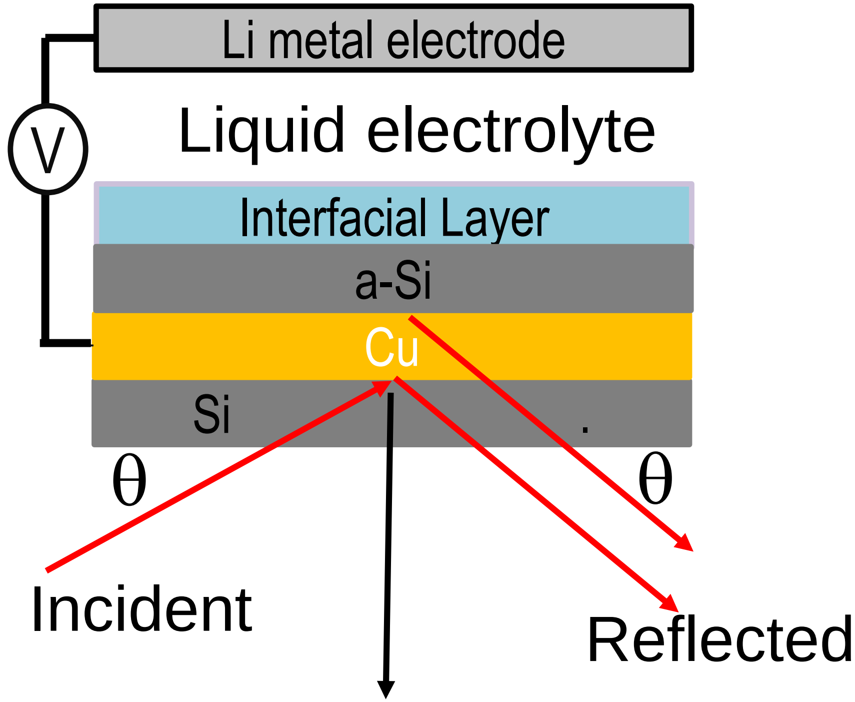
Soaking in electrolyte causes dissolution of well defined SiO_2 coating layer which will change capacity (BAT348)

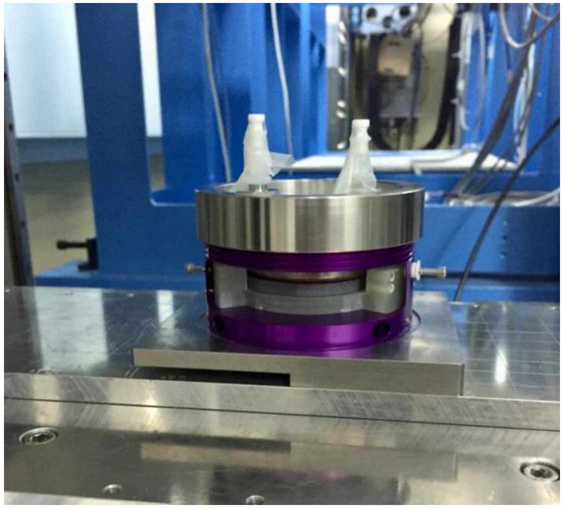


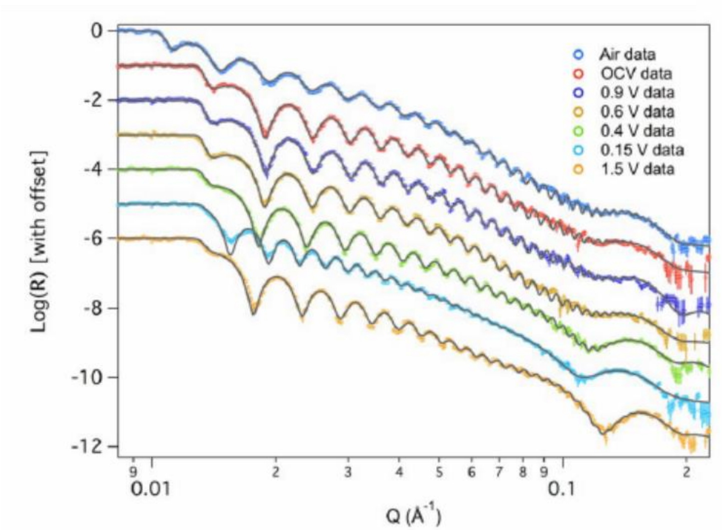
Lithium in bulk is from Li knock on during sputtering



Used neutron reflectometry to follow chemical corrosion influenced by water



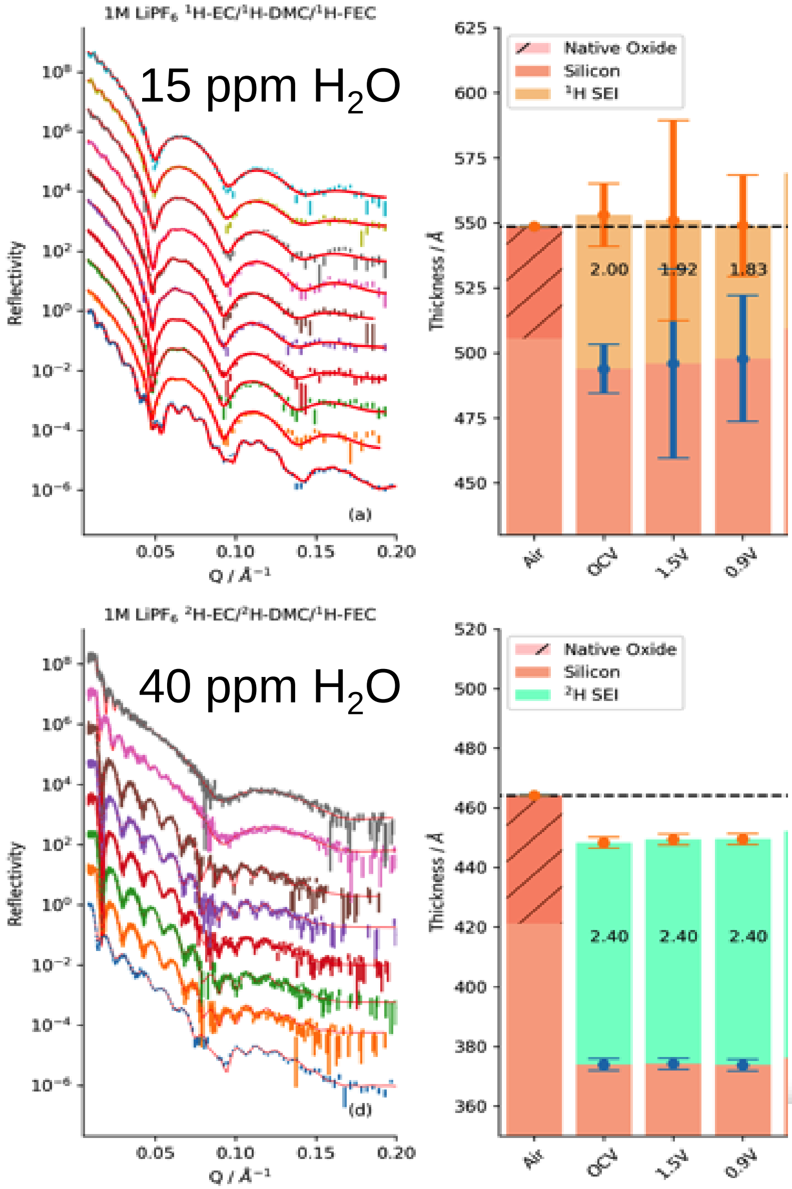




Scientific Reports (2017)

- Used to measure thickness and nuclear composition with time and state-of-charge
- Sensitive to Li and H

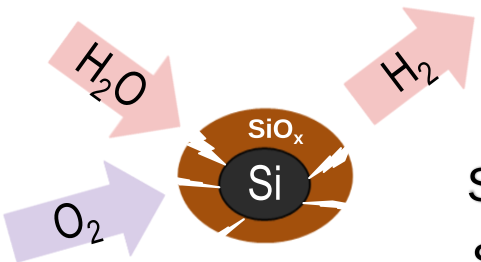
Identified reaction consumes Si immediately after contacting electrolyte



- Upon contact with electrolyte start consuming Si on surface (t = 30 min)
- Addition of water results in enhanced dissolution rate (50 nm vs. 100 nm)
- On a 100 nm particle 10 nm consumption would account for 50% of the theoretical capacity

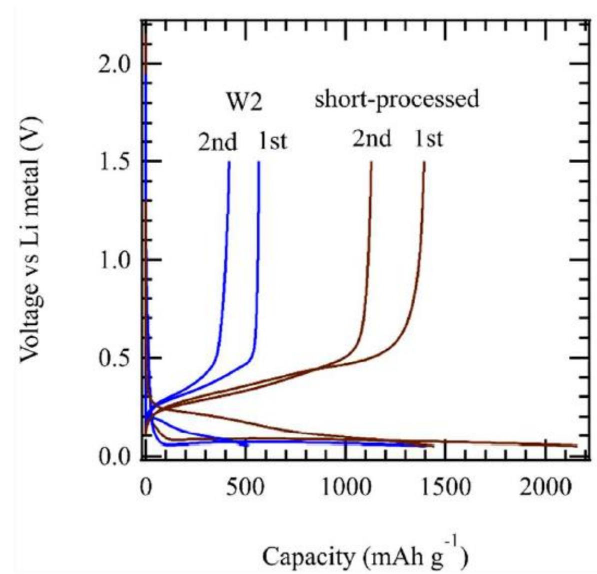
Processing of Si changes surface chemistry

Significant inadvertent changes in surface chemistry due to oxide formation lowers capacity of silicon anode (More in BAT349)



$$Si + H_2O \rightarrow SiO_x + H_2$$

$$Si + O_2 \rightarrow SiO_x$$



- Processing Si in aprotic and protic solvents changes the surface chemistry through:
  - the formation of more oxide
  - decomposition of binder and carbon

Hays *et al.*, submitted to JPC, 2018

Remaining Challenges and Barriers

Long way to go to stabilizing silicon electrodes

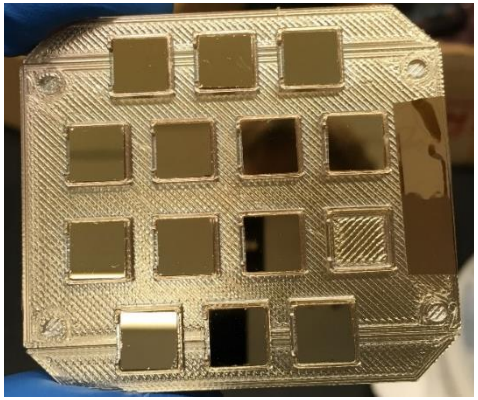
- Starting to get a handle on the influence of surface chemistry on reactivity
- Challenge is to apply this knowledge to designing Si materials
- Exploring changes over multiple length scales
- Developing a time dependent model of reactivity as a function of electrolyte and starting surface composition

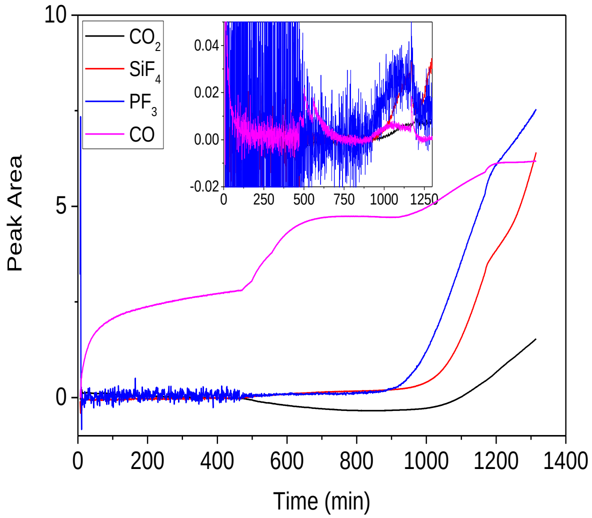
Proposed Future Research Directions

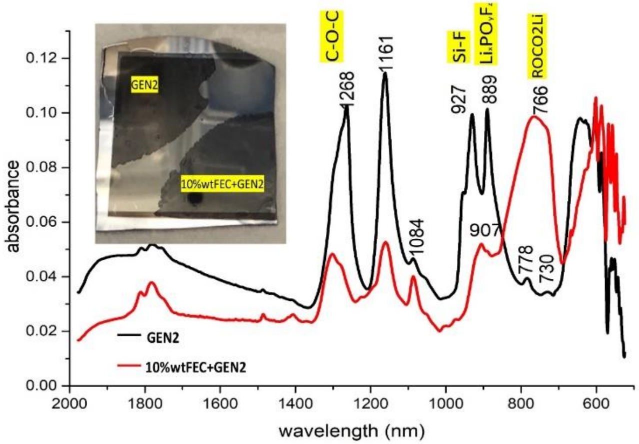
- Further identification of active sites for gassing and electrolyte decomposition
- Start introducing complexity (Binder, carbon black) and ways to neutralize surfaces
- Explore influence of Li-Si-O on ionic transport and SEI formation
- Extend studies to materials that are cycled
  - Directly related to life expectancy of cells

Any proposed future work is subject to change based on funding levels

Summary







Well defined electrodes with known surface chemistry for studies across multiple platforms

Explored gassing products and rates and changes with surface chemistry

Identified surface termination that appear to be stable in electrolyte and how changes affect performance

Contributors and Acknowledgements

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